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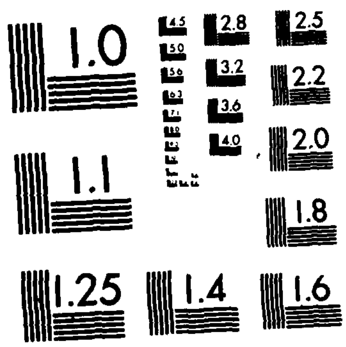

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Annual Report

Feasibility Study on a Process for Electroless Metal Deposition In Pits and Fissures of Teeth for Use in Preventive Dentistry

Thomas J. O'Keefe

February 1983

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Further studies were undertaken to test the feasibility of using metal films deposited by electroless or chemical means for use in dentistry. The areas covered during this year of research were: evaluation of different mordants and wetting agents as substitutes for the etching step, study of parameters affecting adherence between substrate and amalgam, modifications of drying conditions during plating, and optimization of amalgams.

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INTRODUCTION

The main concern during this past year of research has been optimizing the interaction and adhesion between the substrate (silverfoil, ivory, or dentin) and the amalgam. Shear stress testing was the chosen method for evaluation of these tests.

Different mordants were evaluated as possibilities for improving the reproducibility of the shear stress values. Based on some reports of mordant behavior, it was hoped that they could be used as supplementary etching reagents. A study of wetting agents was performed in light of their effects on dentin and evaluating them as possible etching agents. The appraisal of the effects when mordants or wetting agents were used was made using contact angle measurements. Using some of the spherical amalgams that are in the market and silver foil which gives good means of homogeneity as a smooth surface substrate, we searched for the best operating conditions. We went through the study of different parameters affecting the adherence between the substrate and the amalgam plug. The standardization of optimum conditions dealing with Hg concentration and trituration time even within the same kind of amalgam but different batches of it received from the same supplier is fairly important. We obtained very promising results when dry conditions prevail in our system. The effect of dryness in the substrate and the complete standardization for final conditions needs more experimental work but certainly the optimization of each single component in the system will lead us to great security when clinical application arises. The trend of the last chapters in this report show some advances in the optimization of our system.

I. METHODS

The standard electroless plating procedure described as follows has been found to give the best, most reproducible results. The procedure consists of four important stages: etching, pretreatment, prereduction and repetitions.

1. Standard Procedure for Electroless Plating

Substrate: Exposed dentin or polished ivory.

I. Etching

(a) Rinse with demineralized water.

(b) Blot dry (in some instances different drying conditions are used)

(c) 1 min. 50% citric acid in water, natural pH, move Q-tip during etching (dentin); 1 min. 42.5% H_3PO_4 (ivory).

(d) Rinse with demineralized water.

(e) Blot dry or nitrogen-acetone when stated.

II. Pretreatment

(a) 3 min. 50 gpl SnF_2 in water (fresh solution), natural pH, move Q-tip during application.

(b) Rinse with demineralized water.

(c) Blot dry (or left wet without rinsing in some experiments).

III. Prereduction

(a) 1 min. 200 gpl $AgNO_3$ pH 2.85 (let silver solution age 2 days before use - adjust pH with HNO_3), move Q-tip during application.

(b) Rinse with demineralized water.

(c) Blot dry.

(d) Saturated $FeSO_4$ in water, pH adjusted to $\sim$1.8 with

H_2SO_4 before $FeSO_4 \cdot 7H_2O$ addition. Saturation by constant stirring ≥45 min. (fresh solution <8 hours old). Add cysteine to conc. 1 gpl. Apply solution 1 min., move Q-tip during application.

(e) Rinse with demineralized water.

(f) Blot dry or nitrogen-acetone when stated.

IV. Repetitions (9 repetitions)

(a) 10 sec. Ag^+ solution, move Q-tip set it aside.

(b) 30 sec. $FeSO_4$-cysteine soln., move Q-tip.

(c) 20 sec. Ag^+ solution, move Q-tip, same as above.

(d) Rinse with demineralized water.

(e) Blot dry or nitrogen-acetone in the first three repetitions.

2. Drying Conditions

Normally, during plating, the samples are blotted dry after rinsing them with demineralized H_2O between reagent applications.

When using nitrogen-acetone for drying, the drying procedure consists of blowing with nitrogen, then applying acetone with swab and blowing with nitrogen once more.

3. Burnishing

The burnishing is accomplished using the tip of the Dense Condensaire plugger moving it uniformly over the plated surface with a light touch. All the samples used for this report were burnished before amalgamation if nothing else is stated. Note about drying agents: Acetone is miscible in water, so it should assist in removing adsorbed moisture from surface sites. It is volatile and relatively innocuous. Acetone-ether drying solution (V/V) is a blend of low boiling point solvents, when applied to the tooth surface evaporates and the moisture

on the surface will be removed.

II. MORDANTS

Mordants are salts with a multiply-charged cation, Fe^{3+}, Zr^{4+}, or Ti^{3+} and usually the anion is Cl^-. Mordants have been used on enamel and dentin in order to improve the bonding capabilities of the substrate. The cations are believed to replace soluble Ca^{2+} on the substrate surface, thus forming a less water soluble surface. The new cations form stronger chelate complexes than Ca^{2+}. Mordants are also used as a pretreatment to improve fluoride uptake.

Clarkson et al.[1] did a study on enamel with a metal-fluoride pretreatment. They used 0.025M mordant solutions of $FeCl_3$, $TiCl_3$, and $ZrOCl_2$ applied for 30 sec. followed by APF (acidulated phosphate fluoride) application for 150 sec. Their results showed that caries-like lesion was retarded to a greater extent in Mordant-APF treated enamel than in only APF treated enamel. They also found that metal ion mordanting followed by APF application formed amorphous-type coatings.

The SnF_2 pretreatment used in this project could be considered as a mordant too because of the Sn^{2+} ions. The same solutions as described in Ref. 1 were tried as so was 0.025M TiF_3. The mordants were applied after the samples were etched but before the SnF_2 pretreatment. The mordants were applied on ivory and dentin and their influence on shear stress and resistance were tested. Some samples were studied using SEM and x-ray diffraction. Some contact angle measurements on dentin and enamel were done in order to see how the mordants change the adsorption of aqueous solutions onto the substrate. The mordant solutions are very acidic, the pH for $TiCl_3$ being 1.4, $FeCl_3$, 2.1 and $ZrOCl_2$, 2.8.

Pretreatment with mordants and SnF_2 on ivory did not alter shear stress or wear resistance values when compared to SnF_2 pretreatment only (see Table

I). The sample treated with TiF_3 gave the lowest values, which may be an indication of the importance of the anion, Cl^- is preferred to F^-. The results from experiments on dentin are not conclusive because of the large standard deviation (see Table II). The mordants are used as etching agents with or without prior etching with citric acid. Citric acid etching seems necessary on dentin, but more experiments are planned.

TABLE I

The Influence of Mordants on Shear Stress and Wear Resistance

Plating procedure: polished ivory was etched with 42.5% H_3PO_4 for 1 min., 30 sec. 0.025 M mordant followed by 2-1/2 min. 50 gpl SnF_2. $AgNO_3$, 200 g/l and pH 2.8 was applied for 1 min. and then saturated $FeSO_4 \cdot 7H_2O$ + 1 g/l thiourea for 1 min. (=prereduction). The ivory sample was rinsed between every application. The plating was done in 9 repetitions of $AgNO_3$ - $FeSO_4$+ 1g/l thiourea - $AgNO_3$.

Substrate: Ivory

Amalgam: Spheraloy, Sybraloy, Aristaloy

Sample	Shear Stress (psi)		Wear Resistance 10g/2 min
no mordant	1462 ± 617	(4)*	6
0.025 M $FeCl_3$ pH 2.1	1315 ± 395	(4)	6
0.025 M $TiCl_3$ pH 1.4	1320 ± 836	(3)	9
0.025 M TiF_3 pH 2.8	856 ± 520	(4)	5
0.025 M $ZrOCl_2 \cdot 8H_2O$ pH 2.8	1188 ± 703	(4)	7

* Numbers in parentheses show the number of tests

TABLE II

Mordants as Etching Agents on Dentin.

Plating procedure: 1 min. etch, 3 min. 50 gpl SnF_2, 1 min. 200 gpl $AgNO_3$ pH 2.8, 1 min. saturated $FeSO_4$ + 1 g/l cysteine and 9 repetitions of $AgNO_3$ - $FeSO_4$ + cysteine - $AgNO_3$

Substrate: Dentin

Amalgam: Sybraloy

Etching Agent	Resistance after 10x (Ω)	Shear Stress (psi)
1 min 50% citric acid	0.29	485 ± 538 (6)*
1 min 0.025M $FeCl_3$	0.27	275 ± 495 (4)
1 min 0.025M $TiCl_3$	0.28	352 ± 582 (5)
1 min 0.025M $ZrOCl_2 \cdot 8H_2O$	0.27	281 ± 563 (4)
1 min 50% Citric acid + 1 min. 0.025M $FeCl_3$	0.42	81 ± 89 (4)
1 min 50% Citric acid + 1 min. 0.025M $TiCl_3$	0.53	635 ± 378 (6)

*The numbers in parentheses indicate number of tests

III. AMALGAMS

During the last two years, seve ːl different amalgams have been used because of the discontinued production of fine cut Caulk pellets. Fine cut Caulk non-zinc, Aristaloy, Sybraloy and Spheraloy are spherical. Aristaloy and Sybraloy are high in copper, 13 and 30%, respectively, compared to 6% in Spheraloy. It is obvious that the amalgams are going to react differently with a silver surface since a chemical reaction between amalgam and silver occurs. The amounts of mercury differ from one amalgam to the other (see Tables III and IV). All the tests from Tables III to VI are done on silver foil. Silver foil was chosen because it provides a homogeneous, consistent initial substrate, not subject to the variability encountered in plated samples.

In Table III Aristaloy is compared to fine cut Caulk pellets with and without zinc. The optimum amount of mercury was chosen to be 55%, because the consistency was good and the standard deviation was low. The trituration time was 8 sec as suggested by the company. With 55% mercury in the amalgam, a relatively broad ring around the amalgamated area is found. The ring is high in mercury so diffusion has taken place. In Table IV, Spheraloy and Sybraloy are compared to Aristaloy. The conditions are chosen from the optimization studies of Spheraloy in Table V and of Sybraloy in Table VI. The pellets are smaller so two were used.

For optimizing Spheraloy and Sybraloy, both trituration time and amount of mercury were altered. The optimum conditions chosen for Spheraloy were 44% Hg, 5 sec trituration using setting Medium 2 and for Sybraloy, 45% Hg, 10 sec and Medium 2 on a Caulk Vari-Mix II triturator, Model VM-B.

TABLE III

Comparison of Shear Stress Values of Different Amalgams on Silver Foil (a)

Alloy Pellet	Amount of Hg (%)	Trituration time (sec)	Shear Stress (psi)	
Fine Cut Caulk	51	7	1049 ± 392	(3)*
Fine Cut Caulk non-zinc	51	10	1218 ± 481	(3)
Aristaloy	52	8	1435 ± 544	(4)
Aristaloy	55	8	1344 ± 276	(4)
Aristaloy	57	8	1560 ± 559	(4)

* Numbers in parentheses indicate number of tests.

TABLE IV

Comparison of Shear Stress Values of Different Amalgams on Silver Foil (b)

Alloy Pellet	Amount of Hg (%)	Trituration Time (sec)	Shear Stress (psi)
Aristaloy	55	8	649 ± 302 (3)*
Spheraloy (2 pellets)	44	5	534 ± 417 (3)
Sybraloy (2 pellets)	46	10	318 ± 277 (3)

*Numbers in parentheses indicate number of tests.

TABLE V

Optimization of Composition and Trituration Conditions
of Spheraloy on Silver Foil

Amount of Hg (%)	Shear Stress as a factor of trituration time			
	4 sec	5 sec	6 sec	Average
43	600	423	0	341
44	738	981	477	732
45	354	585	400	446
Average	564	663	292	44% Hg 5 sec

Setting: Medium 2 on Vari-Mix II triturator

TABLE VI

Optimization of Trituration Conditions and Composition
of Sybraloy on Silver Foil

Sybraloy pellets are high in copper, 30%

	Trituration Time			
Amount of Hg (%)	9 sec Shear Stress	10 sec Shear Stress	11 sec Shear Stress	Average Shear Stress
45	615	519	481	524
46	246	673	527	493
47	500	462	395	438
Average	454	551	467	45% Hg 10 sec.

Setting: Medium 3 on Vari-Mix II triturator

A) SHEAR STRESS TESTING

The influence of three factors was studied simultaneously: mold size, cleanliness of mercury and condensation method. Two mold sizes were used (1/4 and 3/16 inch diameter). These molds were placed on top of the 0.013 square inch hole to hold the amalgam on the flat sample surface. The 1/4 inch diameter mold gives a thinner amalgam layer than the 3/16 inch diameter mold, since the same amount of amalgam is used. The results are shown in Table VII. There is a very significant difference in shear stress between 1/4" and 3/16" molds, the larger diameter mold giving higher strength. The reason for this difference is not evident. The mold size may play a minor role by changing the stress distribution during testing but it seemed unlikely that it would result in as large a variation as was obtained by increasing the diameter from 3/16 to 1/4 inch diameter.

Comparison of old and new mercury shows a significant difference. The old mercury was exposed to the laboratory atmosphere for several months. It was stored in a dispenser that allows air circulation to some extent. An oxide film covered the surface of the mercury, but it did not contaminate the drops used for the amalgam unless the bulk of the mercury was contaminated too. It is reasonable to believe that the mercury was impure after such a long exposure and the surface layer was an indication of saturation with some foreign substances. The clean mercury had been distilled four times and had never been exposed in the laboratory.

Included in Table VII is a listing which gives the diameter of the visually notable amalgam area present on the silver foil. Mercury diffused out from the amalgamated area and the spread was measured using a manostat. The spread was largest for old mercury and the small diameter mold and the shear stress was poorest. This indicates that there is an excess of mercury at the boundary between the amalgam and the silver foil which causes diffusion.

TABLE VII

Influence of Mold Size and Purity of Mercury on Shear Stress.

Mercury that had been standing ir. lispenser for a few months was compared to mercury that had been distilled four times and not exposed to laboratory atmosphere. Two mold sizes were compared; 1/4" and 3/16" diameters.
Substrate: Silverfoil.
Amalgam: Spheraloy, 2 pellets, 44% Hg, 5 sec trituration time.

Sample Mold Size (inch)	Number of tests	Shear Stress (psi)	Diameter of Mercury ring (mm)
New Mercury 1/4	6	1107 ± 502	5.9 ± 0.2
New Mercury 3/16	6	590 ± 267	5.9 ± 0.2
Old Mercury 1/4	6	496 ± 332	5.6 ± 0.5
Old Mercury 3/16	6	91 ± 152	7.2 ± 0.7

One of the amalgam plugs was studied in cross section using SEM and the energy dispersive x-ray analyzer. The sample was analyzed at approximately 550 μm intervals and the results are shown in Table VIII. There is a gradient of decreasing mercury and increasing silver and copper going from the top of the plug toward the amalgam-silver interface. It appears that mercury is diffusing from silver and copper compounds but not from tin compounds since the concentration of tin remains the same throughout the sample. The amalgam is a low copper amalgam, 6% (Spheraloy).

The influence of condensation conditions on shear stress was tested and the results are shown in Table IX. The standard method for condensation is to divide the triturated piece of amalgam into three equal size portions and condense one at a time on the sample. Another method used for this test was to divide the amalgam into one small and two larger size portions and condense the small one first to get a thin layer. This was done in an attempt to reduce the mercury diffusion by forming a slightly hardened layer before the rest of the amalgam was condensed. The third method inolved three equal size portions of amalgam, the first piece was manually pressed down. During condensation, the amalgam becomes more splashy, less viscous and more shiny which indicates that there is more free mercury; this is avoided during manual condensation.

The results in Table IX show no significant difference for average shear stress but the deviation shows that the values are most consistent when the standard method is used.

The influence of the time of exposure of mercury to the laboratory atmosphere was mentioned earlier. A test was performed after portions of two drops of mercury had been exposed 1, 3 and 6 days in the laboratory and compared to amalgam with mercury that had been stored in a desiccator.

TABLE VIII

Gradient of Cu, Ag, Sn and Hg in an Amalgam Plug.

Energy dispersive x-ray analysis is used. The amalgamation was done on silver foil using a 3/16 inch diameter mold, shear stress was 185 psi.
Amalgam: Spheraloy, 2 pellets, 44% Hg, 5 sec. trituration time.

∿550 μm Intervals	Cu (at.%)	Ag (at.%)	Sn (at.%)	Hg (at.%)
Top Surface	7.18	50.59	17.09	25.14
	6.79	50.12	16.73	26.37
	7.13	50.36	16.40	26.12
	6.72	51.67	16.48	25.13
	7.00	53.24	16.24	23.53
	7.36	53.97	16.86	21.82
Silver-amalgam interface	8.24	53.38	17.11	21.27

TABLE IX

Influence of Condensation Method of Amalgam on Shear Stress.

The test was done in conjunction with the test in Table I, under the same conditions. Standard method is to divide the amalgam in three similar size pieces and condense one at a time. The standard method was compared to a first thin layer from a small amount of amalgam, followed by two larger pieces and to a first manually pressed down amalgam followed by two pieces condensed down onto the silver foil.
Substrate: silver foil
Amalgam: Spheraloy, 2 pellets, 44% Hg, 5 sec. trituration

Sample	Number of Tests	Shear Stress (psi)
Standard, three equal portion	4	729 ± 214
First small and two equal portions	4	891 ± 646
First manually pressed down	4	785 ± 704

The results are presented in Table X. There is no significant difference in shear stress, although the longest exposed mercury resulted in the lowest values. The exposure time was obviously too short (although the surface/volume ratio was much larger than in the mercury exposed for a few months.

An attempt was made to remove excess mercury from the amalgam silver foil interface by touching the first portion of amalgam on an extra piece of silver foil before amalgamation. The tests were timed to determine if the total time of amalgamation influences the results. The results are presented in Table XI and again one can see that the testing conditions have non-significant influences. The control sample was not touched on silver foil before amalgamation and the time was varied; still the average was the highest and the deviation the smallest. The total time of amalgamation does not influence the results when it is kept below 120 seconds. A longer time is not useful since the amalgam hardens very fast and its appearance becomes dry. By touching the amalgam on silver foil before amalgamation some of the mercury reacts because an amalgam spot is left on the foil, but it has no influence on the shear stress values.

TABLE X

Exposure of Mercury 1, 3 and 6 Days to Laboratory Atmosphere and The Effect on Shear Stress.

Substrate: silver foil
Amalgam: Spheraloy, 2 pellets, 44% Hg, 5 sec. trituration time

Sample	Number of Tests	Shear Stress (psi)
Control*	4	900 ± 313
1 day exposure	3	721 ± 323
3 days exposure	3	711 ± 635
6 days exposure	4	688 ± 266

*For the control the mercury was stored in a desiccator.

TABLE XI

Touching of Amalgam on Silver Foil Before Amalgamation To Remove Excess Mercury.

Only the first third of the amalgam was touched. The time dependency was also measured.
Substrate: Silver foil.
Amalgam: Spheraloy, 2 pellets. 44% Hg, 5 sec. trituration time

Sample	Number of Tests	Total Time trituration/ amalgamation (sec)	Shear Stress (psi)	Diameter of Mercury ring (mm)
Control	3	65 - 120	572 ± 114	7.0 ± 0.3
Short Time	3	65 - 75	495 ± 198	6.2 ± 0.4
Medium Time	3	90	515 ± 446	6.8 ± 0.3
Long Time	3	120	492 ± 253	6.6 ± 0.3

B) SPHERALOY

After working with Spheraloy for one year, we are aware of the fact that there are differences in the element composition (Ag, Cu, Sn) from one batch of amalgams to the other, Table XII. All our pellets are from the same supplier. After the arrival of each batch, it is imperative to standardize it for mercury percent and trituration time needed to obtain the optimum conditions for amalgam preparation. This standardization as it is has been stated is done on Ag-foil, which provides a homogeneous substrate to obtain good amalgam adhesion.

Optimization for the 12-5-82 amalgam batch is shown in Table XIII. There are two choices for obtaining good adhesion. One combination is 43% Hg and 4 sec. trituration time and the other is 44% Hg with 4 or 5 sec. trituration time.

In the 2-7-83 amalgam batch where the Sn and Cu content vary to a greater extent, Table XIV, there is a need for a higher amount of Hg to obtain good adhesion on the substrate, Table XIV.

TABLE XII

SEM ANALYSIS

Amalgam pellets. Different batches.

Element & Line	Atomic %		
	6-9-82 (pellets)	12-5-82 (pellets)	2-7-82 (pellets)
Cu Kα	6.62 ± 0.11	7.69 ± 0.08	7.66 ± 0.52
Ag Lα	62.49 ± 0.09	63.10 ± 0.27	63.59 ± 0.48
Sn Lα	30.88 ± 0.04	29.21 ± 0.27	28.75 ± 0.06

TABLE XIII

Optimization of Composition and Trituration Conditions of Spheraloy on Ag-foil (pellets from 12-5-82).

Amount of Hg	Shear Stress (psi) as a Factor of Trituration Time						
(%)	3 sec.	4 sec.	5 sec.	6 sec.	7 sec.	10 sec.	15 sec.
43		953 ± 454(12)	569	0	0	0	
43.5		277					
44	285	800 ± 257(3)	846		115		0
44.5		338					

TABLE XIV

Optimization of Composition and Trituration Conditions of Spheraloy on Ag-foil (pellets from 2-7-83)

Amount of Hg (%)	Shear Stress (psi) as a Factor of Trituration Time 4 sec.	5 sec.	6 sec.
43		292, 62 }177	323
43.5	423	0	
44	338	638	
44.5		723	
45		715	
45.5		477	
46		685	
47	1654	515	
47.5		1438	

IV. CONTACT ANGLE MEASUREMENTS

Contact angle measurements were performed using an NRL Contact Angle Goniometer, Model A-100. A drop of demineralized water was placed on the surface of enamel or dentin. Several drops were measured to get a representative value. The contact angle gives information about the surface, the smaller the angle, the more hydrophilic is the substrate, when comparing aqueous solutions. Without any treatment, the contact angle on dentin is 45.0±5.9 and on enamel 83.2±6.0 (see Table XV). After 1 min. of 42.5% H_3PO_4 etch, the angles are 61.6±8.4 and 0 0, respectively. The properties of dentin are now more hydrophobic, probably because of the removal of the inorganic part of the substrate, leaving the surface amorphous and organic. The drops of water spread immediately over the surface of etched enamel. Organic acids seem to etch dentin better than enamel but their etching properties on enamel can be improved by adding inorganic mordant salts (see Table XV). The organic acids are physiological, as citric acid, and should therefore be less objectionable than inorganic acids from a toxicity standpoint. Succinic and glutamic acid give the lowest contact angles on dentin, but they are not very soluble in water, 68 gpl and 15 gpl, respectively. In the above experiments, 50% solutions were used which meant that these acids were like pastes.

A combination of citric acid and $TiCl_3$ gave the same result on enamel as H_3PO_4, while citric acid by itself is too weak to etch this substrate. By increasing the concentration of inorganic salt in the organic acids, the etching properties should be stronger.

A trial was done to find alternative etching agents to citric acid (see Table XVI). Formic, malic and glutamic acid seem promising. The values are misleading in a way because the control sample etched with citric acid was low in shear stress. Formic acid may be objectionable because it causes skin irritation. The concentrations of malic and glutamic acid are very low

TABLE XV

Contact Angles of Water on Dentin and Enamel After Etching
1 min. with Organic Acids (Biological), Mordants or a Combination of Both

Etching Agent	Dentin		Enamel	
no etch	45.0 ± 5.9	(14)	83.2 ± 6.0	(10)
42.5% H_3PO_4 pH ≤ 0	61.6 ± 8.4	(24)	0 ± 0	
22.3% H_3PO_4 pH 0			0 ± 0	
50% Citric acid pH 0.4	37.7 ± 4.1	(16)	55.5 ±12.1	(14)
25% Citric acid			47.8 ± 3.2	(16)
50% Lactic acid pH 2	40.9 ± 5.5	(16)	56.5 ± 8.9	(12)
Concentrated Lactic acid pH 1.3	40.4 ± 8.9	(24)	32.4 ± 4.3	(16)
50% Oxalic acid pH 1	39.6 ± 7.4	(20)	35.3 ± 4.1	(12)
50% Ascorbic acid pH 2	39.2 ± 7.1	(16)	50.0 ± 6.8	(24)
50% Succinic acid pH 2	30.4 ± 4.6	(18)	49.7 ± 3.5	(16)
50% 2-Glutamic acid pH 6	24.5 ± 7.6	(16)	50.1 ±12.7	(16)
0.025M $FeCl_3$ pH 2.1			59.6 ± 6.8	(16)
0.025M $TiCl_3$ pH 1.4			31.3 ± 8.1	(16)
0.025M $ZrO{\cdot}Cl_2{\cdot}8H_2O$ pH 1.8			44.6 ± 7.2	(16)
22% H_3PO_4 + 0.013M $TiCl_3$			0 ± 0	
25% Citric acid + 0.013M $TiCl_3$			0 ± 0	
25% Lactic acid + 0.013M $TiCl_3$			19.0 ± 3.5	(8)
50% Lactic acid + 0.013M $TiCl_3$			30.4 ± 8.1	(14)
25% Oxalic acid + 0.013M $TiCl_3$			32.7 ± 6.3	(12)
25% Ascorbic acid + 0.013M $TiCl_3$			30.6 ±10.2	(16)
25% Succinic acid + 0.013M $TiCl_3$			41.9 ± 8.3	(16)
25% Glutamic acid + 0.013M $TiCl_3$			42.0 ± 3.0	(16)
25% Citric acid + 0.013M $FeCl_3$			40.8 ± 4.9	(16)
25% Lactic acid + 0.013M $FeCl_3$			33.3 ± 3.9	(32)
25% Oxalic acid + 0.013M $FeCl_3$			42.2 ± 8.4	(24)

* Numbers in parentheses indicate number of measurements.

TABLE XVI

Different Organic Acids as Etchants on Dentin, Their Influence on Shear Stress.

The samples were etched 1 min. and plated using standard conditions,

50 gpl SnF_2, 200 gpl $AgNO_3$ pH 2.8, saturated $FeSO_4$ + 1 gpl cysteine.

Substrate: Dentin

Amalgam: Sybraloy

Etchant	Resistance (Ω) 10x	Shear Stress (psi)
50% Citric acid	0.54	254 ± 133 *
22.5% Formic acid	0.34	1090 ± 633
5% Malic acid	0.60	732 ± 145
7% Succinic acid	1.05	331 ± 573
0.5% Aspartic acid	0.23	613 ± 580
1.5% Glutamic acid	0.65	587 ± 257

* No peeling. The silver layer peeled off partly from all other samples but the one etched with citric acid.

because of their low solubility. These acids need further investigation, using higher concentrations which means that they are going to be paste-like but that they may be desirable from an application point of view. Succinic and aspartic acid gave acceptable average shear stress values but the deviation shows that some of the amalgams fell off before testing. The silver layer peeled to some extent from all samples but the one etched with citric acid. So far, the standard procedure for plating gives the best test results but efforts are made to improve the properties and to obtain more homogeneous results.

Wetting Agents and Contact Angles

Wettability is considered necessary for a fluid material to adhere to a solid. Wettability also measures a fluid's ability to displace other liquids and gases and to spread over the surface so as to produce an interface without voids. Wetting phenomena involves forces of attraction between adhesive molecules and those of the tissue (adherend) (dentin).

Treatment of the substrate (dentin) with wetting agents was thought to offer possibilities for enhanced bonding. A dry substrate surface usually seems to provide for good penetration into dentin and better adsorption by the solutions. Alternatively, the wetting agents might allow for increased contact of the dentin by the metal ions.

The etching step removes cutting debris blocking tubule entrances and facilitates penetration of substances into the tubules. Etching is not fully recommended due to the possible harsh effect of acids commonly used and a further non-favorable pulp response. The use of lower acid concentrations may offer some improvements; a shear stress value of 1892 psi when using 6.25% citric acid indicates this. A combination of dry substrate conditions and treatment with a wetting agent might substitute the etching step leaving the substrate prepared for further steps, possibly allowing the proper formation of anchoring tags for silver adhesion.

The criteria used to find a suitable wetting agent was on the basis of the main effect it would produce on the collagenous-mineralized structure of dentin.

Several substances tested dealt mainly with: demineralization, breaking of H-bonds, attraction of opposite charges, solubilization of collagen, etc. Table XVII summarizes them, giving some aspects of their effects and uses.

One way to evaluate the wetting effect obtained on dentin is by the contact angle. Contact angle measurements can be employed to monitor the properties of solid surfaces, e.g., the degree of wetting, surface contaminants, surface roughness, etc. The contact angle was measured on dentin surface obtained after polishing the teeth on a diamond wheel and 600 grit emery paper. Contact angle measurements were performed using a NRL Contact Angle Goniometer, Model A-100. Demineralized water was placed on the dentin surface and the contact angle measured to obtain a representative reference value. Each tooth used was its own control, measuring the contact angle before treatment with the substance under study, Table XVIII.

The average normal value obtained for contact angle on dentin in our laboratory conditions is around 45. Contact angle values of 0-15 denote noticeable changes in the properties of the dentin surface, indicating mainly a strong molecular attraction promoting an important physical and chemical change. Dentin properties became more hydrophilic. Triton X-100, 10% Sparkleen and conc. MICRO, being surface active agents gave contact angle values denoting good wetting properties for dentin (0-12.21 θ).

TiF_4 that acts especially forming complexes with organic material, turned out to be partially effective, lowering the contact angle about 50% from the control value.

Dodecyl sulfate and urea with specific effects on the collagenous

TABLE XVII

WETTING AGENTS

$CaCl_2$	Will bring collagen into solution.
EDTA	Demineralization dentin; Solubilizes non-collagenous organic matrix components of dentin.
Ethylene glycol	Wetting agent used in plastics; Absorbs twice its weight of water at 100% relative humidity.
Glycerin	Wetting agent in plastics.
H_2O_2	Effective cleanser agent of teeth.
Dodecyl sulfate sodium salt	Unique protein denaturant; Shows electrovalent reaction of its long chain like anion with the cationic protein groups; Dissociates polypeptide chains.
Micro	Liquid laboratory cleaner; Has a solubilizer, anionic and nonionic surface active agents.
Photo Flo 600	Wetting agent for photographic use.
Sparkleen	Detergent generally used as a surface active agent.
TiF_4	Ti^{+4} forms different complexes with organic material.
Triton X-100	Non-ionic surfactant; wetting agent.
Urea	Breaks hydrogen bonds; denaturalizes proteins.

TABLE XVIII

CONTACT ANGLES MEASURED AFTER TREATMENT WITH WETTING AGENTS

Time of Treatment	Wetting Agents	Contact Angles: Control	Contact Angles: After Treatment
2 min.	2M $CaCl_2$	29.16±1.94 (6)	30.88±5.62 (8)
2 min.	20% EDTA	40.25±3.72 (14)	34.44±7.69 (14)
4 min.	20% EDTA	40.25±3.72 (14)	31.46±4.37 (14)
2 min.	Ethylene glycol	28.75±4.24 (6)	30.07±4.75 (14)
2 min.	Glycerin	31.79±4.61 (14)	31.29±4.66 (14)
2 min.	H_2O_2	33.82±5.28 (14)	29.14±3.89 (14)
2 min.	10% Dodecyl sulfate sodium salt	43.25±3.01 (16)	22.56±2.03 (16)
2 min.	20% MICRO	51.78±6.56 (14)	47.38±4.05 (12)
2 min.	Conc. MICRO	51.78±6.56 (14)	12.21±4.39 (14)
2 min.	Photo-Flo 600 (1:200)	41.58±5.37 (12)	26.00±4.71 (13)
2 min.	10% Sparkleen	33.46±3.57 (14)	11.14±8.18 (14)
1 min.	2% TiF_4, pH 2.21	52.00±3.84 (14)	25.43±6.00 (14)
2 min.	Triton X-100 (1:100)	49.25±5.80 (12)	0
2 min.	6M Urea	39.71±5.62 (14)	26.32±5.47 (14)
4 min.	6M Urea	39.71±5.62 (14)	26.21±3.42 (14)

Note: Numbers in parenthesis denote number of angle measurements.

composition of dentin proved to be active to some extent.

In a preliminary test measuring the shear stress in a sample treated with Triton X-100 (1:100 diln.) as a substitute of etching, the value obtained was low (662 psi) but it may be desirable to perform more experiments.

The possibility of obtaining good attachment tags when working with wetting agents applied at the same time as the SnF_2 was attractive, even though the preliminary shear stress value is low (600 psi) but more testing is needed considering the etching step is avoided these results give some indication of good adhesion.

V. STUDIES ON IVORY

Plating Procedure "A" on ivory includes: 1 min etch with 42.5% H_3PO_4, 3 min pretreatment with 50 gpl SnF_2, 1 min with 200 gpl $AgNO_3$ pH 2.8, 1 min saturated $FeSO_4$ + 1 gpl thiourea and 9 repetitions of $AgNO_3$ (10 sec) - $FeSO_4$ + cysteine (30 sec)-$AgNO_3$ (20 sec) on polished substrate. The sample is rinsed with demineralized water between each step. The solutions are applied with cotton swabs saturated in them.

These conditions have been used in the next series of experiments, Tables XIX, XX, and XXI.

Influence of Different Operators on the Shear Stress

The results are collected from different experiments over a six month period (see Table XIX). The results show that the difference between operators is insignificant compared to the standard deviation of the values on each sample. From the table one can see that burnishing the electroless plated silver layer with the amalgam condenser has a positive effect on the shear stress.

These tests can be done only one at a time, so as to avoid mercury diffusion from the amalgamated area to the surrounding silver layer, it was made discontinuous. The ivory samples were covered with electroplaters tape in which holes had been punched; the holes were of the same size as the amalgamated area usually is. The last three samples in Table XIX are plated in the described manner. The results are satisfactory but not significantly higher than the others which means that the method with a continuous silver layer still can be used.

Effect of Solution Volume

Unless otherwise mentioned in the different experiments, the cotton swabs have always been saturated with plating solution. The amount of

TABLE XIX

Standard Procedure for Plating Ivory, Three Operators

Polished ivory was etched with 42.5% H_3PO_4 for 1 min., 3 min. 50 gpl SnF_2, 1 min. 200 gpl $AgNO_3$ pH 2.8, 1 min. saturated $FeSO_4$ + 1 gpl thiourea followed by 9 repetitions of $AgNO_3$ - $FeSO_4$ + thiourea - $AgNO_3$

Substrate: Ivory

Amalgam: Aristaloy, 55% Hg

Sample	Resistance (Ω) 10x	Shear Stress		
Operator I	0.71	470 ± 470	(5)*	one piece
Operator I burnished[a]	0.71	802 ± 267	(5)	
Operator II	0.14	1172 ± 697	(5)	one piece
Operator II burnished[a]	0.19	1492 ± 436	(6)	
Operator II	0.55	734 ± 1068	(6)	
Operator II	0.51	141 ± 72	(4)	
Operator III	0.27	1049 ± 637	(6)	
Operator III		563 ± 402	(4)	
Operator I[b]		1171 ± 174	(5)	
Operator II[b]		1241 ± 606	(6)	
Operator I[c]		708 ± 368	(4)	

a)After plating the sample was burnished with the amalgam condenser

b)Discontinuous Ag film on ivory (every amalgamated area was separated). Amalgam: Sybraloy 47% Hg

c)Discontinuous Ag film as in b. Amalgam: Spheraloy 45% Hg

* The numbers in parentheses indicate number of tests

TABLE XX

Influence of the Degree of Saturation of the Cotton Swabs Used in Plating on Shear Stress and Wear Resistance

Plating was done using standard conditions for ivory: H_3PO_4 etch, SnF_2 pretreatment, prereduction with 200 gpl $AgNO_3$ and saturated $FeSO_4$ + 1 gpl thiourea. Followed by 9 repetitions of Ag^+ - Fe^{2+} - Ag^+.

Substrate: Ivory

Amalgam: Precapsulated Spheraloy, 50% Hg

Sample	Resistance (Ω) 10x	Shear Stress (psi)		Wear Resistance
Saturated Q tip I[a]	0.31	438 ± 153	(3)*	5
Saturated Q tip II	0.08	277 ± 53	(2)	5
0.20ml in Q tip I	0.86	187 ± 62	(3)	0
0.20ml in Q tip II	0.90	427 ± 158	(2)	0
0.15ml in Q tip I	11.6	46 ± 41	(3)	0
0.15ml in Q tip II	6.4	38 ± 66	(3)	0

a) I and II indicate two different operators.

* Numbers in parentheses indicate number of tests.

Table XXI

Drying samples at different stages of electroless plating using nitrogen and acetone.

Silver plating: Plating procedure "A", with 200 gpl $AgNO_3$ pH 2.85
Substrate: Ivory
Amalgam: Spheraloy, 2 pellets, 44% Hg, 5 sec. trituration time, M-2 setting.

Drying	Number of Tests	Shear Stress (psi) Individual values	Mean & St. dev.
before 1 min. 42.5% H_3PO_4	3	1708, 1262, 838	1269 ± 435
before 3 min. 50 gpl SnF_2	3	2454, 1908, 1792	2051 ± 354
before 1 min. 200 gpl $AgNO_3$ pH 2.85	3	1469, 1292, 1169	1310 ± 151
before 1 min. sat. $FeSO_4$ + 1 gpl Cysteine	3	1885, 1085, 2038	1669 ± 488
before first Ag^+-Fe^{+2}-Ag^+	3	2015, 1062, 1723	1600 ± 488
before all $AgNO_3$ applications	3	2631, 2269, 1915	2272 ± 358
before every step	3	2485, 1085, 2038	1869 ± 715
control*	3	1154, 754, 1177	1028 ± 238

* Blot dried before every step.

Note: Every sample was burnished before amalgamation.

solution in a saturated cotton swab is not known, but if more than 0.2 mol is available, everything is not absorbed. There is a significant difference in resistance and wear resistance between the samples plated with saturated and non-saturated cotton swabs while the shear stress does not seem to be as sensitive unless the amounts of solutions are very limited as in the swabs with 0.15 ml, Table XX. In the conditions presently used, the swabs are immersed in bottles containing the plating solutions and thus, the degree of saturation is dependent on the level of solution. The plating conditions can be standardized even more if the amount of solutions are fixed.

Effect of Degree of Dryness in the Plating Process

It was felt that adsorbed surface moisture could be detrimental to the plating process and subsequent amalgam adherence. A series of experiments was made using ivory as substrate and intercalating drying steps through the plating procedure (Table XXI). In the table, it is specified where the drying is performed using nitrogen which is blown on the substrate surface, then applying acetone with a swab and blowing with nitrogen once more. The results show that the relative dryness of the substrate is decisive in determining good adherence between the substrate and the amalgam. There is also definite difference in grain size and deposit in each sample, as was confirmed by SEM.

Due to the fact that dry conditions have a positive effect on shear stress, these were adopted and intercalated in the plating procedure "A". The samples are always (nitrogen-acetone) dried in the following stages of plating unless a modification is stated: before the SnF_2 application, before first one minute with 200 gpl $AgNO_3$ and before the three first repetitions from the nine with Ag^+-Fe^{+2}-Ag^+.

TABLE XXII

Ivory

Modifications on Standard Procedures and Effect on Shear Stress

Modifications	Exp. No.	Drying with N_2-Acetone-N_2 (Before)	Drying with N_2-Acetone-N_2 (During)	Shear Stress (psi)	No. of Tests
Without SnF_2; No cysteine	1	Prereduction		431 ± 122	4
Without SnF_2; Cysteine	2	Prereduction		850 ± 268	4
AgF all steps; 1 min AgF before SnF_2 (Pretreatment)	3	a) AgF b) Pretreatment c) Three first repetitions	Prereduction	135 ± 81	4
AgF all steps; 1 min AgF before SnF_2 (Pretreatment); Prereduction twice	4	a) AgF b) Pretreatment c) Prereduction d) Three First Repetitions		1419 ± 612	5
AgF (Prereduction); $AgNO_3$ (Repetitions)	5	a) Pretreatment b) Three First Repetitions		1272 ± 461	3
AgF before SnF_2 (Pretreatment); AgF (Prereduction), $AgNO_3$ (Repetitions)	6	a) AgF b) Pretreatment c) Three First Repetitions	Prereduction	541 ± 340	3
AgF in all steps; Standard Procedure with modified drying conditions	7	a) Pretreatment b) Three First Repetitions		2252 ± 319	4

Modified Conditions in the System

After the preliminary studies on ivory, using drying conditions, some additional alterations to the process were attempted. The following list describes these changes.

(a) Elimination of the additive and SnF_2 to check the effects on the properties.

(b) Using AgF instead of $AgNO_3$.

(c) Using AgF for all Ag^+ applications.

(d) Applying AgF before pretreatment.

(e) Using AgF and $AgNO_3$ in the same procedure. AgF before pretreatment; AgF prereduction; $AgNO_3$ repetitions.

(f) AgF applied before and after pretreatment.

(g) SnF_2 applied on dry sample.

(h) SnF_2 left as solution on tooth surface without rinsing or blot drying for next step.

(i) Several sequential SnF_2 applications.

(j) Prereduction step done twice.

Table XXII summarizes the results obtained on ivory after the modifications to the system. Cysteine and SnF_2 are shown to be essential in the procedure. When AgF was applied before SnF_2 to check if Ag^+ reduction could be improved, this did not happen, but if it is applied before SnF_2 and then the prereduction is performed twice, this condition makes the Ag^+ available for reduction. When Ag^+ is delivered as AgF and $AgNO_3$ in the same system, experiments 5 and 6, Table XXII, the AgF application before SnF_2 pretreatment was not beneficial, giving a shear stress about one-half the normal value. Experiment 7 in Table XXII shows the best shear stress values were obtained when using AgF in all steps and employing the drying conditions.

VI. STUDIES ON DENTIN

Plating Procedure "A" on dentin includes: 1 min etch with 50% citric acid; 3 min pretreatment with 50 gpl SnF_2; 1 min 200 gpl $AgNO_3$ pH 2.8; 1 min saturated $FeSO_4$ + 1 gpl cysteine followed by 9 repetitions of $AgNO_3$ - $FeSO_4$ + cysteine - $AgNO_3$. The samples are rinsed with demineralized water between each step and after each repetition. The plated samples are stored in demineralized water overnight, prior to the first amalgamation. A test was run to study the influence of storing conditions in dentin samples before amalgamation of dentin, Table XXIII. The results show that there is no significant difference between samples stored overnight in water or air or if they were amalgamated immediately after plating.

All the following tests performed on dentin denote effects on the shear stress determination chosen at the present stage of the project as the expression of an adequate interaction and adhesion between substrate, Ag surface, and amalgam.

Amalgamation Procedure

The dentin surface is dried cleaned with acetone using a swab and blown dry with nitrogen. A piece of masking tape with a 0.013 square inch hole is applied on it and a mold with 1/4 inch diameter is placed on top matching the hole and secured in place with masking tape. After proper cleaning of capsule, as it will be stated, two pellets of Spheraloy (Kerr) alloy are mixed with 44% of mercury dispensed by the SYBRALOY/SPHERALOY proportioner and placed on a Caulk Vari-mix II triturator for 5 seconds at medium 2-speed. Then the amalgam is divided into three equal sized portions and condensed one at a time on the sample with Densco Condensaire plugger which is driven by nitrogen at 30 psi. The samples are set and allowed to harden in demineralized H_2O at room temperature for one hour and aged at 37°C to complete

TABLE XXIII

Influence of Storage Conditions Before Amalgamation of Dentin

Standard conditions for plating dentin: 1 min. 50% citric acid, 3 min. 50 gpl SnF_2, 1 min. 200 gpl $AgNO_3$ pH 2.8, 1 min. saturated $FeSO_4$ + 1 gpl cysteine followed by 9 repetitions of $AgNO_3$ - $FeSO_4$ + cysteine - $AgNO_3$.

Substrate: Dentin

Amalgam: Aristaloy, 55% Hg

Sample	Resistance (Ω) 10x	Shear Stress	
1 day in H_2O, Operator I	0.40	1115 ± 365	(4)*
1 day in H_2O, Operator II	0.44	977 ± 223	(3)
1 day in air, Operator I	0.57	1215 ± 565	(3)
1 day in air, Operator II	0.21	243 ± 203	(3)
No storage, Operator I	0.50	1108 ± 716	(4)
No storage, Operator II	0.37	1043 ± 618	(4)

* Numbers in parentheses indicate number of tests

24 hours before the shear stress test is accomplished.

Trituration Conditions

Analyzing some of our preliminary results when optimizing different available amalgams, we see in the case of SYBRALOY (30% copper), higher shear stress values when a different new plastic capsule is used for each trituration (Table XXIV). If the same plastic capsule is reused, the shear stress diminishes. It was desirable to have a smooth and clean inner surface after each trituration. Several methods were used to clean the capsules, some of them are time consuming, making the process impractical. Finally, we adopted the method of using Q-tips to wipe the inside and afterwards blowing with nitrogen to remove dampness. Our cleaning method is proper and we have confidence in reusing the same capsule as it is presented in Table XXV.

Conditions for Amalgam Aging

When the amalgam alloy is triturated with mercury, the particles of the alloy absorb the mercury, and a decrease in the total volume occurs by this absorption, giving place to a contraction; this is called "dimensional change". This contraction occurs during the first hour after condensation. We chose three different conditions (Table XXVI) and keeping the samples in demineralized water at room temperature for this first hour is favorable. The samples were at 37°C to complete the 24 hours before testing the shear stress.

We were not sure if a change in lot of Spheraloy pellets was going to affect our results. We tested comparatively the two lots of amalgam, obtaining no variation due to this fact, Table XXVII.

Silver Amalgam Boundary

In an attempt to remove excess mercury from the amalgam-silver dentin

Table XXIV

Different capsules for trituration

Substrate: Silver foil
Amalgam: Sybraloy, 2 pellets, 47% Hg; 10 sec. trituration time; M-3 setting

Capule Used	Number of Tests	Shear Stress (psi)
New for each determination	4	556 ± 189
Same	4	371 ± 74

Table XXV

Different capsules for trituration.

Silver Plating: Standard Conditions
Substrate: Dentin
Amalgam: Spheraloy, 2 pellets, 44% Kg; 5 sec. trituration time, M-2 setting.

Capsule Used	Number of Tests	Shear Stress (psi)
New for each determination	3	916 ± 215
Same	4	1275± 333

Note: All samples were burnished before amalgamation.

Table XXVI

Amalgamated samples kept in different conditions during the first hour after their completion.

Silver Plating: Standard Procedure
Substrate: Dentin
Amalgam: Spheraloy; 2 pellets; 44% Hg; 5 sec. trituration time, M-2 setting

Condition for first hour	Number of Tests	Shear Stress (psi)
In air at room temperature	4	800 ± 499
In H_2O at room temperature	4	1275 ± 333
In H_2O at 37°C	3	433 ± 382

Note: All samples kept in H_2O at 37°C to complete 24 hours of aging.

Table XXVII

Shear stress tests using two different lots of Spheraloy (Kerr)

Silver plating: Standard conditions
Substrate: Dentin
Amalgam: Spheraloy, 2 pellets, 44% Hg, 5 sec. trituration time, M-2 setting.

Spheraloy(Kerr) lot	Number of Tests	Shear Stress (psi)	
I	7	962 ± 474	962 ± 418
II	8	962 ± 398	

Note: All samples were burnished before amalgamation.

interface different means were used: a) touching the first portion of amalgam on an extra piece of silver foil before amalgamation, b) adding Ag powder obtained from amalgam pellets so the excess mercury will combine and lessen its diffusion and c) electroplating the electroless Ag plated dentin surface. The results are presented in Table XXVIII and we can see the highest variability is obtained when Ag powder is added in the interface. The control sample did not have additions in the interface and gave higher shear stress values. Apparently, the excess mercury is not affecting now the adherence amalgam-substrate.

Light for Prereduction

Another external factor that would not affect the composition of our system but might improve its conditions is using light to prereduce the silver. It is known that a very small quantity of reduced silver is an excellent catalyst for silver salts obtaining an enhanced rate of metal deposition. Photoprereduction was performed at different stages of plating. It was concluded it is not a factor that will improve our methods. Table XXIX shows the numbers.

Effect of Degree of Dryness During Plating on Shear Stress Values

Dentin samples mounted horizontally and blotted dry during plating gave good shear stress values. The shear stress values are higher if dentin is exposed vertically where the access of reagents to tubular walls is easier as it is seen in Table XXX. The tendency to get greater shear stress values is confirmed when samples are dried with nitrogen-acetone.

Modified Conditions in the System

In Table XXXI we have a compilation of results of studies using dentin as the substrate and working with modified special drying conditions which are: drying with nitrogen-acetone before the SnF_2 application, drying before

Table XXVIII

Attempt to remove excess mercury from the amalgam-silver dentin interface by: 1) Touching the first portion of amalgam on a piece of silver foil before amalgamation. 2) Addition of Ag powder from a pulverized amalgam pellet on Ag plated surface. 3) Electroplating the electroless Ag plated surface.

Silver plating: Standard procedure.
Substrate: Dentin.
Amalgam: Spheraloy (Kerr) 2 pellets; 44% Hg; 5 sec. trituration time; M-2 setting

Conditions	Number of Tests	Shear Stress (psi)
1)	4	343 ± 395
2)	3	476 ± 616
3)[a]	11	743 ± 383
Control*	4	1275 ± 333

* Direct adherence between Ag plated dentin surface and amalgam

a Electroplating conditions: 50 gpl AgF; 300 gpl KSCN (pH 2.85); ∿30-40 mA/cm^2 during 2-5 min.

Note: All samples were burnished before amalgamation.

Table XXIX

Using Photoreduction at different stages of electroless plating.

Silver plating: Standard conditions.
Substrate: Dentin
Amalgam: Spheraloy, 2 pellets, 44% Hg, 5 sec. trituration time, M-2 setting

Photoreduction	Number of Tests	Shear Stress (psi)
One step[a]	4	973 ± 213
Several steps[b]	6	1164 ± 572
Control (without light)	1	1500

a) Light applied to sample at 1/2 inch from source during 1 min. after 1 min. of 200 gpl $AgNO_3$ pH 2.85.

b) Light applied to sample in the same conditions as in a) and before all further reagent applications in the plating procedure.

Note: All samples were burnished before amalgamation.

Table XXX

Drying procedure during electroless plating and the effect on shear stress.

Substrate: Dentin
Amalgam: Spheraloy, 2 pellets, 44% Hg, 5 sec. trituration time, M-2 setting.

Sample	Drying Procedure	Number of Tests	Shear Stress (psi) Individual Values	Mean & St. dev.
Teeth horizontally mounted	Blotting	32	a) lowest is 277 b) 5 tests <900	1124 ± 345
	N_2-Acetone before 1 min. $AgNO_3$ and every further step.	6	300, 1362, 1854, 1854, 1208, 2269	1475 ± 690
	N_2-Acetone before every step	6	608, 600, 969 1231, 969, 1085	910 ± 256
Teeth vertically mounted	Blotting	8	2130, 1554, 1438, 1438, 1969, 1015	1731 ± 446
	N_2-Acetone before every Ag^+ application	6	1885, 1246, 2262, 962, 1915, 1015	1548 ± 543

Note: All samples were burnished before amalgamation.

the one minute application of 200 gpl $AgNO_3$ and drying before the first three repetitions with Ag^+-Fe^{+2}-Ag^+. The conclusions from the study compiled in Table XXXI are the following:

Using AgF and $AgNO_3$ in the same system does not improve the shear stress values. Ag^+ applied as AgF throughout the entire procedure gave acceptable values but not significantly better than with $AgNO_3$. Some more tests should be performed in the light that when using AgF in all steps on ivory as substrate gave fairly high shear stress numbers. A 3 min SnF_2 pretreatment leaving it as a solution on the tooth, omitting the normal following rinsing-drying and adding the $AgNO_3$ for 1 min on wet SnF_2 made the shear stress values quite variable with values from 477 to 2038 psi being obtained.

The best conditions were obtained using $AgNO_3$ during all steps of the procedure and applying SnF_2 on a dry substrate, having in the system the modified dried conditions.

Range of Shear Stress Values with Different Batches of Amalgam

The processing conditions used to prepare the amalgam appear to be very critical. Large variations in results have been obtained among various batches of amalgam pellets, even when purchased from the same supplier. The small variations in concentration of the amalgam components (Cu, Ag, Sn) require careful choice of trituration time and Hg concentration to obtain the best conditions for our plug preparation, and best attachment to our substrate.

The range of adhesion in a control tooth at standard conditions (1 min. 50% citric acid; nitrogen-acetone dry; 3 min. 50 gpl SnF_2; nitrogen-acetone dry; 1 min 200 gpl $AgNO_3$; rinse and blot dry; 1 min. sat. $FeSO_4$ + 1 gpl cysteine; nitrogen-acetone dry before the 3 first repetitions; 9 repetitions of $AgNO_3$-$FeSO_4$ + cysteine - $AgNO_3$) is 387±128 psi with the amalgam pellets received on 12-5-82. It is considered low if we compare it with the range

1461 ± 300 psi for dentin in a control tooth at standard conditions using amalgam pellets from the 6-9-82 batch.

A large group of low shear stress values was unavoidable. The effects of varying the citric acid, $AgNO_3$ and SnF_2 concentrations to find an optimum, the change of $FeSO_4$ to ascorbic acid as reducing agent, the application of SnF_2 before etching and the use of dry samples by different procedures to start plating, were examined considering the low control value range for dentin.

The lower concentration of citric acid was tested as an etching agent assuming it would supply less harsh conditions for the clinical use of the system. Examining the results from Table XXXII, it is noted that when lowering the citric acid concentration from the 50% concentration usually used to 6.25%, gave a slight increase in shear stress values (experiments 2 and 4, Table XXXII); 6.25% citric acid for etching and 25 gpl SnF_2 instead of 50 gpl SnF_2 and 100 gpl $AgNO_3$ instead of 200 gpl $AgNO_3$ also increased the shear stress values, experiment 4, Table XXXII. But if 50 gpl SnF_2 remained in the system with lower $AgNO_3$ concentration (100 gpl) the effect was not very noticeable (experiment 3, Table XXXII). The purpose of lowering the $AgNO_3$ was to find the optimum concentration for silver for the system. The positive effect obtained when the SnF_2 concentration was diminished indicates that the optimum concentration is lower than 50 gpl SnF_2.

The conductivity measurement indicates the uniformity of the silver film on the substrate. In Table XXXII, the sample for experiment 3 shows a high conductivity number in the second silver layer, probably affecting the subsequent deposit. In general, a final conductivity lower than one is acceptable.

Combining a mild etching treatment with a different reducing agent or with a previous application of SnF_2 in the tooth was thought as a beneficial

TABLE XXXI

DENTIN

MODIFICATIONS ON STANDARD PROCEDURE AND EFFECTS ON SHEAR STRESS

Modifications	Shear Stress (psi)	Maximum and Minimum Values	Number of Tests
$AgNO_3$ all steps; SnF_2 kept wet for Prereduction	1100±647	2038; 477	6
AgF (Prereduction); $AgNO_3$ (Repetitions)	910±104	1015; 808	3
AgF before SnF_2 (Pretreatment); $AgNO_3$ (Repetitions)	461±133	538; 308	3
AgF all steps; 1 min. AgF before SnF_2 (Pretreatment); 1 min. AgF after SnF_2 (Pretreatment)	1289±409	1615; 692	4
AgF all steps; 1 min. AgF before SnF_2 (Pretreatment); SnF_2 left wet for Prereduction; 2 more SnF_2 (Pretr) followed by 1 min. AgF with SnF_2 left wet	1092±186	1315; 862	4
$AgNO_3$ all steps; Std. procedure with modified drying conditions.*	1461±300	1892; 977	19

Note:

1) Samples were always nitrogen-acetone dried for AgF before Pretreatment.

2) Drying steps: Before Pretreatment, Prereduction and three first Repetitions.

3) All samples dried with nitrogen-acetone but*.

4) *Dried with nitrogen-acetone-ether.

TABLE XXXII

VARIATIONS ON STANDARD PROCEDURE AND EFFECTS ON SHEAR STRESS

Substrate: Dentin

Amalgam: Spheraloy; 44%, 5 sec

Exp. Number	Variations	Shear Stress psi	No. of Tests	Ω 2X	Ω 10X
1	Control (50% citric acid) 50 gpl SnF_2; 200 gpl $AgNO_3$	387 ± 128	3	11.42	0.45
2	6.25% citric acid; 50 gpl SnF_2; 200 gpl $AgNO_3$	692 ± 288	3	8.48	0.39
3	6.25% citric acid; 50 gpl SnF_2; 100 gpl $AgNO_3$	503 ± 302	3	306.00	0.76
4	6.25% citric acid; 25 gpl SnF_2; 100 gpl $AgNO_3$	938, 669 } 804	2	12.84	0.44
5	6.25% citric acid; 25 gpl SnF_2; 200 gpl $AgNO_3$	923, 0 } 462	2	22.74	0.77

Note: - start with blot dry teeth.

- pH for $AgNO_3$ soln. is 2.85.

- all samples were dried with N_2-acetone before SnF_2 and before 1X, 2X and 3X (repetitions).

TABLE XXXIII

REDUCING AGENTS. INFLUENCE ON SHEAR STRESS.

Substrate: Dentin

Amalgam: Spheraloy; 44% Hg, 5 sec trituration time

Exp. No.	System Conditions	No. of Tests	Ω 2X	Ω 10X	Shear Stress psi
1	Control. 50% citric acid; 200 gpl $AgNO_3$; $FeSO_4$ 1gpl Cysteine	3	11.42	0.45	387 ± 128
2	6.25% citric; 100 gpl $AgNO_3$; 150 gpl Ascorbic + Cysteine	2	175.35	0.59	215, 92 } 154
3	6.25% citric; 50 gpl SnF_2 before and after etch	3	15.53	0.48	379 ± 18
4	6.25% citric; 50 gpl SnF_2 before etch	3	14.07	0.65	574 ± 393

Note: In Exp. 2, 100 gpl $AgNO_3$ and ascorbic acid used in prereduction; for repetitions 2X and 3X, 100 gpl $AgNO_3$ and $FeSO_4$ + 1 gpl Cysteine and repetitions 4X to 10X 200 gpl $AgNO_3$ and $FeSO_4$ 1gpl Cysteine. Experiments 3 and 4 were performed with standard procedure with the changes stated in this table.

step to provide enhanced penetration for the reduction thus improving the strength and adherence of the Ag deposit. Table XXXIII, experiment 2, shows there is no improvement in shear stress values if ascorbic acid is substituted for $FeSO_4$ (reducing agent normally used in the standard procedure). In the same Table XXXIII, experiment 4 suggests a SnF_2 application before etching is beneficial.

It has been established that a dry substrate surface at some stages in the plating procedure usually seems to provide for good penetration into dentin and better adsorption for solutions.

Certainly, more experiments with dry conditions should be done to obtain more consistency which not only depends on the conditions of dryness for the substrate, but in other factors such as penetration into the substrate of the working area and optimum conditions in the plating and amalgamation system.

Conclusions

In an overview of data, it is felt that the chemical plating conditions are good so far. The dry conditions should be tested more in order to reach the desired consistency. The state of the mercury is important. The careful optimization of each amalgam batch is imperative.

REFERENCE

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